III.A.12 SOFC Anode Materials Development at PNNL

Olga Marina (Primary Contact), Jeff Stevenson
Pacific Northwest National Laboratory
P.O. Box 999, MS K2-44
Richland, WA 99352
Phone: (509) 375-2337; Fax: (509) 375-2186; E-mail: Olga.Marina@pnl.gov

DOE Project Manager: Lane Wilson
Phone: (304) 285-1336; E-mail: Lane.Wilson@netl.doe.gov

Objectives

- Develop solid oxide fuel cell (SOFC) anode compositions which will satisfy advanced anode requirements including redox tolerance, sulfur tolerance, and carbon tolerance while offering low polarization losses and long-term stability.
- Improve understanding of mechanisms affecting anode performance, including both intrinsic factors (e.g., composition, microstructure) and extrinsic factors (e.g., S poisoning).

Approach

- Synthesize, process, and characterize candidate SOFC anode compositions.
- Utilize carefully controlled SOFC testing (half-cell and full-cell) to quantify performance of anode compositions under SOFC exposure conditions.
- Evaluate effects of redox cycling and exposure to sulfur compounds and hydrocarbon fuels on anode performance.

Accomplishments

- Demonstrated improved sulfur tolerance for Pacific Northwest National Laboratory's (PNNL's) ceramic composite anode relative to traditional nickel/yttria-stabilized zirconia (Ni/YSZ) SOFC anodes.
- Improved understanding of roles played by ceria and titanate phases in composite anode.

Future Directions

- Evaluate performance and stability of ceramic anode in various hydrocarbon fuels.
- Improve mechanistic understanding of effects of sulfur and carbon on anode performance.

Introduction

The current state-of-the-art anode material is a Ni/YSZ cermet (a composite of Ni metal and YSZ ceramic). Overall, this material offers many good properties, including high electrical and thermal conductivity, reasonable thermal expansion, and chemical and dimensional stability in the fuel gas environment. While Ni/YSZ is satisfactory for cells operating on clean, reformed fuel, advanced SOFC designs are likely to place additional constraints on the anode, such as tolerance of highly oxidizing environments and/or the capability of tolerating significant quantities of sulfur and/or hydrocarbon species in the fuel stream. Ni/YSZ anodes are not stable in oxidizing environments at high temperature. To simplify SOFC system requirements, it is desirable that the anode material be stable not only while exposed to the fuel environment during operation, but also when exposed to more oxidizing conditions (i.e., air) during system startup and shutdown.

Previous work at PNNL has resulted in the development of a promising 2-phase ceramic anode based on a mixture of doped strontium titanate and doped ceria. Optimized compositions in this system offer excellent dimensional and chemical stability during redox cycling, appropriate coefficient of thermal expansion (CTE), and good electrocatalytic activity towards hydrogen reduction. Stable performance with 25 ppm H_2S present in a hydrogen fuel stream was also demonstrated.

Approach

Composite ceramic anode powders in the Sr-La-Ti-Ce-O system were prepared (both by single-step co-synthesis and by mixing separately prepared powders) by glycine/nitrate combustion synthesis. The powders were calcined and then attrition milled to reduce the average particle size to less than 0.5 μm. The resulting powders were characterized by dilatometry, x-ray diffraction (XRD), energy dispersive spectroscopy (EDS), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). Electrode inks were prepared by mixing the powder with a commercial binder in a 3-roll mill, and then screen-printed in a circular pattern onto YSZ pellets or membranes. The screen-printed electrodes were sintered in air at 900-1000ºC. A platinum paste current collector grid was screen-printed on the top of the electrode.

The cells were mounted between two vertical alumina tubes and isolated from the environment by sealing with gold rings when heated to 900ºC in air. After that, fuel was introduced into the anode compartment to reduce the anode. The opposite side of the cell was supplied with air. Experiments were performed at atmospheric pressure in the temperature range 550-900ºC. Electrochemical measurements were carried out using a Solartron 1280 frequency response analyzer in combination with a Solartron 1286 potentiostat or an Arbin BT4 potentiostat.

Results

Electrolyte-supported single cells (160 μm 8YSZ electrolyte) with ceramic anodes were tested in fuel gas containing 290-1000 ppm H_2S over 500 hours; results are shown in Figures 1-3. It was found that

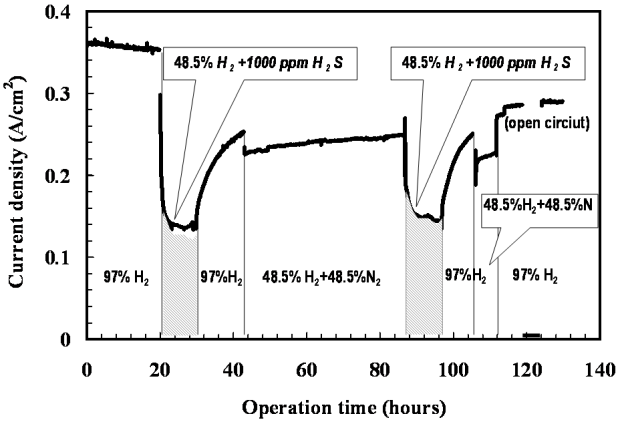

Figure 1. Effect of H_2S additives on performance of the 160-μm YSZ electrolyte-supported cell with La-doped $SrTiO_3$/La-doped ceria composite anode (prepared in one synthesis step) and lanthanum strontium ferrite (LSF20) cathode with a samarium-doped ceria (SDC) interlayer. T=850°C. Cell voltage =0.7 V.

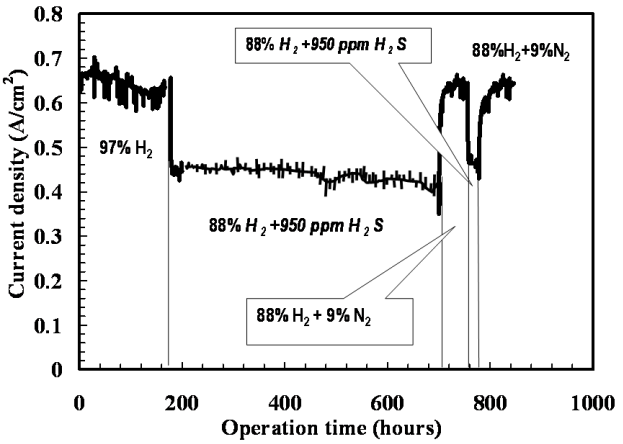

Figure 2. Effect of H_2S additives on performance of the 160-μm YSZ electrolyte-supported cell with a $La_{0.35}Sr_{0.65}TiO_3/Ce_{0.7}La_{0.3}O_{1.85}$ composite anode (prepared by mixing of the oxides in a 7:3 mole ratio) and LSF20 cathode with a SDC interlayer. T=850°C. Cell voltage = 0.3 V.

the cell performance decreased by 40% in the presence of 1000 ppm H_2S (Figure 1) at a cell voltage of 0.7 V, by 30% in the presence of 950 ppm of H_2S at a cell voltage of 0.3 V (Figure 2), and by only 9% in the presence of 280 ppm of H_2S at a cell voltage of 0.3 V (Figure 3). When H_2S was removed from the fuel stream, the composite anodes self-recovered without requiring cleaning with either hot

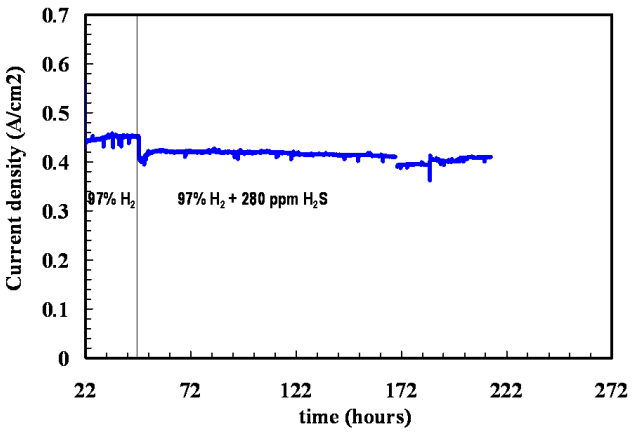

Figure 3. Effect of H_2S additives on performance of the 160-µm YSZ electrolyte-supported cell with a $La_{0.35}Sr_{0.65}TiO_3/Ce_{0.5}La_{0.5}O_{1.75}$ composite anode (prepared by mixing of the oxides in a 5:5 mole ratio) and LSF20 cathode with a SDC interlayer. T=850°C. Cell voltage = 0.3 V.

air or hot steam. Visually, no sulfur deposits were found on the anodes after cooling in H_2. Some yellowish deposits were found on the alumina test fixture. After returning to clean moist hydrogen, some performance decrease (up to 18%) was noticed. This degradation may be related to: i) Pt current collector poisoning due to Pt_xS formation (visual color change was observed), ii) partial Pt current collector delamination from the anode, iii) ceramic anode degradation in the presence of H_2S, and/or iv) cathode degradation with time. It should be noted that no degradation in the anode performance with time in wet hydrogen was observed in half-cell measurements.

Conclusions

Composite ceramic anodes show better stability of performance than Ni/YSZ anodes when H_2S is present in the fuel stream. Studies are in progress to more fully ascertain the conditions under which performance degradation occurs, and the specific mechanisms which lead to degradation.

FY 2004 Publications/Presentations

1. OA Marina, MS Walker, JW Stevenson, "*Development of Ceramic Composites as SOFC Anodes*," in 2003 Fuel Cell Seminar: Fuel Cells - Reliable, Clean Energy, November 3-7, 2003, Miami Beach, Florida. pp. 340-343. Fuel Cell Seminar, Washington, DC.

2. OA Marina, JW Stevenson, LR Pederson, "*Development of Ceramic Composites as SOFC Anodes*," Invited speaker at 55th Pacific Coast Regional & Basic Science Division Meeting of the American Ceramic Society, October 20, 2003, Oakland, CA.

3. OA Marina, "*Development of Advanced SOFC Anodes*," presented at the SECA Core Technology Program Review Meeting, May 11-13, 2004, Boston, MA.